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A Study of Fiber-to-Fiber Flocculation in Pulp Suspensions

Pamela Peay

Western Michigan University

A STUDY OF FIBER-TO-FIBER FLOCCULATION IN PULP SUSPENSIONS

by

Pamela Peay

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ABSTRACT

Fiber to fiber flocculation in pulp suspensions was studied and the influencing factors were discussed. The existence of a microfloc was proposed to explain the behavior of flocculation versus time and degree of agitation. An experimental procedure to quantitatively describe the flocculation and its relationship to time and degree of agitation was not found. Polaroid photography, SLR photography, and a photocell and light source were the attempted methods.

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An important characteristic of finished paper is its formation and look-through. Generally, there are two important factors recognized which affect formation and look-through, flow conditions in the headbox and the degree of flocculation of the suspension as it is deposited on the wire. Fine-to-fiber and filler-to-fiber flocculation in paper is favorable but most fiber-to-fiber flocculation is not and as many factors influence these equally a trade-off must be realized where good fine-and-filler-to-fiber flocculation is maintained at the same time as fiber-to-fiber dispersion.

An excess of fiber-to-fiber flocculation in a sheet will cause a variety of problems including poor strength characteristics, local basis weight variations and an overall poor appearance.

The state of flocs ranges from very stable and resistant to break up to unstable and easily redispersed according to the character of their formation. The easily redispersed flocs have been termed 'soft' flocs and those more resistant to breakup are termed 'hard' flocs.[1] In a pulp suspension flocs are continuously forming and redispersing. A dynamic equilibrium is achieved when the rate of formation of aggregates is equal to the rate of their destruction.

Flocculation is influenced by a number of factors involved in a fiber-water suspension and these parameters must be considered when trying to alter and control the degree of flocculation present in a system. These parameters include consistency, velocity, turbulance, water type, pH, temp-

erature and/or viscosity, beating, fiber type, air, fines, fillers, and polymer or electrolyte addition. The most important of these are turbulance and polymer or electrolyte addition.

An increase in consistency results in an increase in flocculation.[2] This is due primarily to an increased number of fiber-to-fiber collisions.

In a steady state condition an increase in velocity will cause an increase in flocculation up to a point of limiting velocity.[3] This is also due to more fiber-to-fiber contacts.

Turbulance is randomly directed, localized flows within a large flow stream, i.e. eddy currents. Turbulance is short-lived. It's rate of decay is governed by its size or scale. The size of eddy currents is known as the scale. The velocity of their flow relative to the overall stream is the intensity. When fibers are subjected to turbulance the eddy currents create shear forces at intersections with fiber flocs.[4] If the turbulance has a low intensity the flocs may resist breakup. If the turbulance is large whole flocs can exist within a given eddy. By the time the eddy has broken up into smaller ones its energy (the intensity of the small scale turbulance generated) can be too low to break up the larger flocs initially enveloped. Turbulance not only destroys but also creates flocculation by bringing more fibers in contact with each other. It has been shown that flocs in suspension subject to turbulance have an equilibrium size.[5] Decreasing the intensity of the turbulance or increasing the scale causes an increase in the aggregate sizes. In general, it can be said that changes in flocculation follow changes in the turbulance level.[6]

The water type used in a suspension is another parameter which influences the flocculating behavior of the system. Flocculation occurs to a

greater extent in distilled water than in tap water.[7] This is due to reactions occurring with the calcium and magnesium ions in tap water.

PH is another contributing factor. However, pH alone is not enough to characterize a system. PH, a measure of only the hydrogen ion concentration, does not measure the influence of other contributing ions in the solution.

According to Erspamer[8], an increase in viscosity, or a decrease in temperature, should decrease the flocculating ability of a pulp suspension. When the viscosity increases the frictional pull on the fibers is increased and, therefore, an increasing tendancy for dispersion takes place. This is substantiated by Wollwage also.

The effects of beating on the flocculation of a pulp suspension have been found to be related to the specific area of the surfaces involved. Valcik and Komorova[9] found that in the case of a kraft stock, flocculation was enhanced by fibrillating beating and reduced by fiber shortening. Fibrillating beating results in a fiber with more specific area than does cutting.

Wollwage said,[10] that for the same amounts of beating, the comparitive flocculating tendancies of pulps in decreasing order were sulphites, krafts, bleached sulphites, and soda pulps. Due to a more hydrophilic surface of sulphite pulps they are more beatable and have a higher specific surface than kraft pulps resulting in a higher flocculating tendancy.

Flocs of stiff southern pine fibers are more difficult to break up than those of thin-walled more flexible northern fibers.[11] Since each fiber is bent locally at many points during flocculation, fibers exert forces on

one another in direct proportion to their stiffness. These mutual forces of bending cause flocs to have considerable mechanical strength. This is supported by LaMer and Smellie[12] who said that the rate of disintegration of spherical particles is inversely proportional to the surface area of the particle.

The flocculation of a suspension increases as a result of an increased content of air in the system.[13] The factor influencing this is the change in the specific weight of the fibers caused by adsorption of gas. The fibers tend to sink or rise in a standing stock suspension depending on their specific weight. Surface tension and the forces between the phases (water-gas in the form of a bubble) influence this flocculation also.

Increasing the amount of fines in a system increases flocculation.[14] With more area the entrapment and entanglement ability of the network is increased.

Filler addition has been found to have no effect on fiber-to-fiber flocculation.[15]

The addition of electrolytes or polyelectrolytes has been found to increase flocculation. The rate of flocculation with electrolytes is, according to LaMer, Victor, and Smellie[16], dependant on the extent of adsorption, order of mixing, and character of agitation.

Flocculation is increased with the addition of polymers. Cationic polymers appear more effective in flocculation than either anionic or nonionic as seen in the way that agitation affects flocculation.[17] Only cationic polymers interacted with the cellulose strongly enough to maintain flocculation increases at higher agitation. Studies on cationic, anionic, and nonionic polymers retained by fibers indicate that the cationic charge is

adsorbed by the negative cellulose, no adsorption of anionic or nonionic polymers was observed. In the case of flocculation with polymers pH has an effect. Generally, the pH follows the charge state of the polymer functional groups with a pH of five being more effective for cationic polymers. A pH of nine is more effective for anionic or nonionic polymers.[18] Increases in the molecular weight of the polymers were found to cause increases in flocculation, according to Makushina and others.[19]

There is no one known mechanism for flocculation. Flocculation has been found to occur through basically three different mechanisms. These are physical entanglement, charge neutralization, and polymer bridging. The first process involves only mechanical interaction and the last two involve chemical interactions.

The first mechanism is physical entanglement. When fibers collide they become entangled due to their long length. This type of fiber flocculation is easily disrupted by shear forces.

The second mechanism uses the charges present in the system to explain flocculation. In water, cellulose fibers acquire negative charges on their surfaces.[20] This is the result of selective adsorption of ions on the surfaces or the dissociation of electrically active groups.[21] The electrical charge in the paper-stock system primarily influences the proximity of approach of particles and molecules. The negatively charged particles develop an electric double layer and repel each other so that adsorption or flocculation that would otherwise occur is prevented.[22] In the absence of an electric charge barrier to the approach of particles to each other, flocculation occurs. Ionic material and charged colloids present in a system are attracted or repelled by the negatively charged fibers depending

on the sign of the charge.[23] The adsorption of this material changes the surface potential of the fibers and their flocculation behavior. In this way the electrokinetic potential of the electric double layer can be overcome and an effective collision occurs promoting flocculation. This is called charge neutralization. With charge neutralization occurring Van der Waals attraction forces can aid in flocculation formation.[24] Without agents to strengthen this attachment the fibers are easily redispersed using shear forces. These are soft flocs.

The last flocculation method proposed is termed polymer bridging. Two types of bridging are theorized, bridging by which two particles are connected by the ends of a polymer chain, proposed by LaMer and Healy,[25] and bridging through loops and tails, proposed by Fleer and others.[26] In both of these types the mechanism is the same. In the mechanism a segment of a polymer chain is adsorbed onto the surface of a particle. This particle approaches another having a vacant adsorption site and a bridge forms by sorption of the free end of the polymer onto the vacant site.[27] This eventually creates a network that produces a floc.

One would think that negatively charged polymer chains would not be adsorped because they would be repelled by the negatively charged fibers. However, just the opposite has been shown. To explain the flocculating tendancy of some negative colloids, such as starch, according to their bridging theory LaMer and Healy stated:[28]

> ....equilibrium state is controlled by interactions of a chemical nature. The chemical interactions which operate in flocculation are very intense at short range and are of sufficient magnitude to overwhelm the electrostatic repulsion between particles having net charges of the same sign.

Therefore polymer bridging can take place regardless of the sign of the charge on the polymer molecules.

The adsorption of the polymer onto the surface of the fiber particles increases with an increase in the surface area of the particles. This increased adsorption causes an increase in the polymer bridge strength.[29]

The bridging mechanism produces hard flocs which are more resistant to shear forces than those produced by physical entanglement or collision and charge neutralization. However, with increased shear forces and extended exposure flocculation is reduced to a primary level.

As noted earlier, LaMer,[30] Victor and Smellie found that the rate of flocculation was dependant on the order of mixing and the character of the agitation. This was investigated by Goossens and Luner.[31] They found using cationic ionene halide polymers, that with increased time of agitation as well as degree of agitation, more polymer was needed to flocculate the suspension . Based on the polymer adsorption theory and the effect of molecular weight on the flocculation they concluded that the mechanism for this flocculation could best be explained by the 'patch model'. Flocculation is induced by the attraction between positive and negative sides of particles and partial neutralization of the particle takes place. They said the increase in stability against flocculation with time and degree of agitation is caused partially by the release of Ca ions from the surface of the particles, due to polymer adsorption, as well as by the diffusion of polymer into the pores of the particles. Both of these would cause a decrease in the charge of the positive patches on the particles and, therefore, the distance of interaction between two sites on different particles would be increased. Since flocculation depends on the magnitude and distance of

the charges, the particles are less attracted to one another and flocculation decreases.

Muhonen and Williams[32] also noticed a decrease in flocculation with increased time and degree of agitation. They found evidence that the degree of flocculation of a pulp suspension depended on the shear history of the specimen. That is, prolonged slow mixing formed flocs which were hard to disperse at increasing velocities. However, after dispersion, the flocs did not form as readily as a pulp sample that had not been subjected to dispersion. They explained this behavior as follows. During dispersion the flocs are broken up due to destruction of the polymeric bridges and physical entanglement. The destruction of the bridges, they concluded, was an irreversible process and only the flocculation due to physical entanglement was recovered when the mixing speed was slowed down.

Jayme and Muriy[33] also noticed something similiar to this. The degree of nonuniformity of test sheets formed at different time intervals between stirring and sheet formation was determined. Their results showed a linear increase in wildness, or flocculation, of the sheet with increasing time intervals between stirring and sheet formation for all pulps tested. They did not offer any explanation for these results.

The decreased flocculation with increases in time and degree of agitation has not been completely explained by the mechanisms and theories of LaMer, Victor, and Smellie; Goossens and Luner; or Muhonen and Williams. These results can be explained more completely with the hypothesis of the existence of a 'microfloc'. A microfloc is a very small floc which initiates flocculation in a pulp suspension. Microflocs provide active sites where flocculation can develop and these sites are somewhat resistant to agitation.

They are not dispersed with low rates of agitation probably due to their small size. However, when severe and prolonged agitation is present, microflocs are dispersed. After dispersion, time is needed for their reformation before flocculation can occur again.

Microflocs are forming in periods of quiescence and also periods of mild agitation. This is due to an increased number of contacts with other fibers. This hypothesis is consistant with the results seen in the literature. It can also explain the results found on the structure of certain flocs using a sectioning technique.[34] Some flocs, preserved in gelatin, showed a central torsion, a threadlike or 'spun' structure. Cross and longitudinal sections of these flocs showed a twisted central core that was apparently independant of the surrounding fibrous portion. When this technique was applied to non-spun flocs no such twisted portions were observed. These flocs could have been formed by physical entanglement.

Using the hypothesis of a microfloc helps to explain more completely what is happening to the state of flocculation as influenced by increased time and degree of agitation in apulp supension. By a more thorough understanding of the mechanisms involved in flocculation a better control of the problem can be realized.

Experimental Work

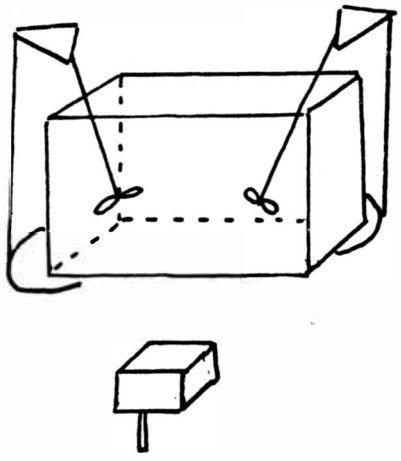
The hypothesis states that a microfloc exists which initiates flocculation by providing sites for flocculation to develop. With mild agitation these microflocs, due to their small size, are not broken up and flocs begin to form as soon as agitation is stopped. With severe agitation these microflocs are dispersed and time is needed for their reformation before flocculation can develop, i.e.,a small induction period is present after agitation is stopped before flocs begin to form.

If this is true then a relationship should exist between the amount of flocculation and time, for both mild and severe agitation. As a result of the literature study the following variables were picked to study flocculation versus time: consistency, temperature and fiber type.

I found that in the time frame of my work I couldnot find a quantitative method of measuring the amount of flocculation with time. The following paragraphs describe attempts to find an experimental procedure to yield a quantitative description of flocculation versus time.

Photography was the first approach. Photographs of the state of flocculation would allow calculation of the percentage of flocculation at different times by counting the number of flocs per unit area and comparing this to previously made standards which would represent 0,10,20,40,60,80, and 100% flocculation. These standards would be prepared using a known flocculant, such as alum. Figure 1 shows this experimental setup.

Figure 1



The vessel containing the fiber suspension must not be too narrow or shear effects from the walls would interfere with the flocculation. However, with a wider vessel the depth of field is too large for the flocs to be distinguishable on a photograph. Therefore, after agitation an opaque glass was inserted into the suspension, just prior to taking the photograph, to give the smaller depth of field necessary. The glass would unavoidably introduce shear effects. If these shear effects are assumed to be the same for each photograph then relative comparisons can be made without introducing effects of shear forces.

Using a polaroid camera with high speed (4000 series) black and white film the photographs were not detailed enough to pick out individual flocs or groups of flocs. Therefore, a change was made to a SLR, single lens reflex, camera which might give more detail. A Minolta XG-7 with Ilford black and white film was used. These photographs also did not distinguish flocs. Therefore several changes were made to increase the contrast: 1.) A telephoto lens, which acts somewhat like a magnifying

glass by bringing the image up closer, was used.

2.) Tungston lighting was used.

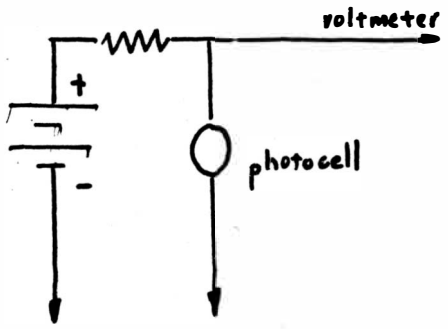
3.) The film was switched to Kodak hi-copy contrast film.

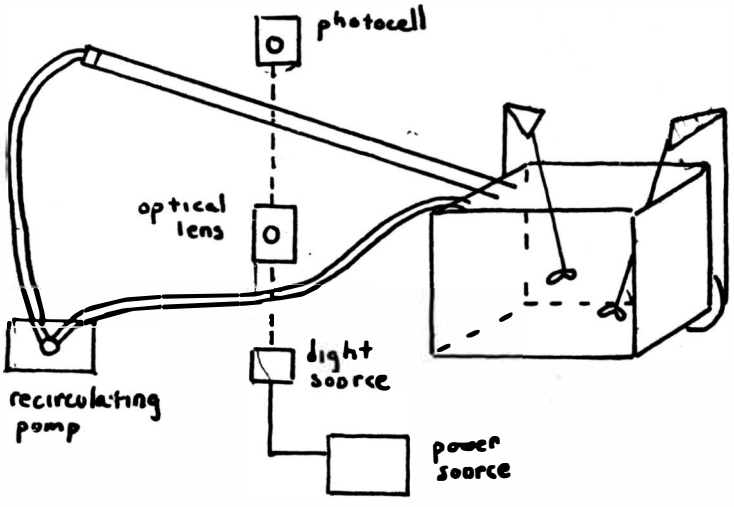
With these changes flocs were still undetectable on the photographs. A conclusion was made at this point that photography was not an acceptable method for this experiment.

In previous literature studies a photocell and light source had been used to study flocculation. The light source transmits a beam of light through the solution and this light is detected by the photocell on the opposite side. If nothing blocks the light beam the photocell receives all of the incident light. If the light beam is partially blocked this causes a change in the intensity of the light beam which is detected by the photocell. This change can be seen numerically if the photocell is connected to a voltmeter. When a well-dispersed system is used, with little flocculation, the voltmeter reading should be essentially constant. With flocculation present, the larger size of a floc, as compared to a fiber, would result in an increased blockage of light decreasing the intensity seen by the photocell and this should be apparent on the voltmeter readout. Figure 2 shows this setup.

By changing the speed of the pump the flocculation can be studied versus time. The light source is a 10-watt point light source. This concentrates the light beam to a point. An optical lens is used to insure that the light beam is of the same diameter throughout the solution. The photocell is shielded in black to prevent interference from room lighting.

Figure 2





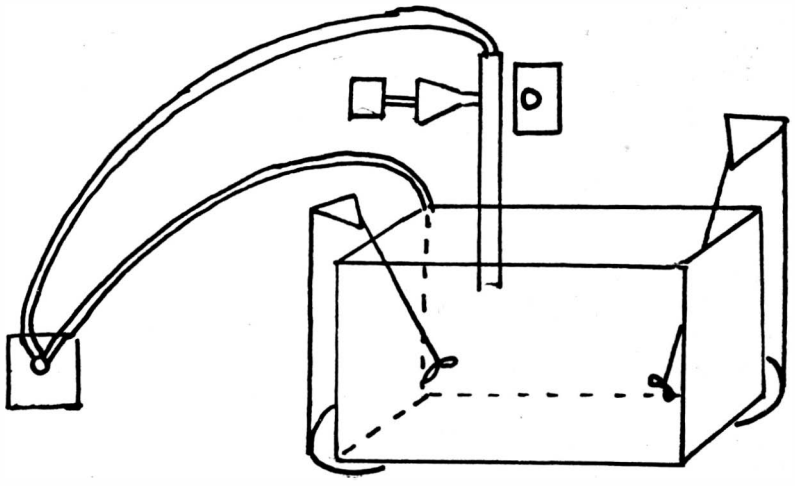
A two-inch plastic pipe is used. Although shear forces are present at the walls of the pipe these are assumed to be constant throughout the experiment and can be neglected in comparisons. A 10,000 ohm resistor is placed in series with the photocell and these are connected to the voltmeter which reads AC volts. The maximum capacity of the pump is 2 liters per minute or .8"/sec. Two mixers are placed at opposite ends in the ten gallon tank to insure uniform mixing.

There were three problems with this setup: 1) The fibers began to settle to the bottom of the tube and gather in plugs so that a plug of fibers would pass the photocell and

then a plug of water and so on, 2) even with a dispersed system the light beam was not powerful enough to pass through the fibers to the photocell, and 3) the consistency had to be held within a small range to avoid pluggage in the pump and total light blockage. A consistency of .05% was optimum and .1% was too high.

The problem with the narrow range of consistencies eliminated the use of consistency as a variable. To solve the first two problems the experimental setup was changed to Figure 3.

Figure 3



Having the tube vertical eliminated the fibers settling out and building up into plugs. The light source was a more difficult problem. Since a point light source could not be found with a higher wattage bulb, a funnel was used to tunnel down an ordinary 100-watt light to a point. However, with

or without the optical lens this light was too diffuse to transmit a beam through the suspension. This was replaced with a 25- watt bulb with a smaller surface area. With the funnel and photocell flush against the pipe and a slightly larger opening in the funnel, this transmitted a powerful beam of light through the suspension which was picked up by the photocell.

When only water was run through the system the voltmeter read 0 indicating that none of the light had been blocked and also the tube walls had no effect on the light beam. With a .05% consistency of 400 CSF softwood the voltmeter read 1.2 volts. By changing the speed of the pump different times can be studied. According to theory, flocculation should increase with time. However, the flocculation showed no change with time. This can be explained with the response time of the photocell. The response time was not quick enough to perceive a change in light intensity as a floc flowed past the light beam. That is, even though a change occurred in the light source it was not apparent in the reading on the voltmeter. To resolve this problem a photocell with a better response time must be used.

Qualitatively, the flocculation appeared to increase with time using the variables consistency and temperature. Looking at fiber types, softwood versus hardwood, at .05% consistencies, it was difficult to see any difference between the two.

To evaluate the flocculation versus time accurately a

quantitative method seems essential. One can see general trends in the flocculation with time but it is impossible to determine what types of relationships exist between the two without quantitative data and this would necessitate the use of a photocell with a faster response time.

The response time of the voltmeter may also be too low to respond to small changes in intensity. Therefore, in further work it is recommended that a photocell and/or voltmeter with a faster response time is used. This would result in an accurate quantitative description of the flocculation as a function of time and degree of agitation.

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